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On-Road Remote Sensing of Automobile Emissions in the Denver Area: Year 4, January 2003

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EXECUTIVE SUMMARY

The University of Denver has completed the fourth year of a multi-year remote sensing study in the Denver area. The remote sensor used in this study is capable of measuring the ratios of CO, HC and NO to CO₂ in motor vehicle exhaust. From these ratios, we calculate the percent concentrations of CO, CO₂, HC and NO in the exhaust that would be observed by a tailpipe probe, corrected for water and excess oxygen not involved in combustion. Mass emissions per mass or volume of fuel can also be determined. The system used in this study was configured to determine the speed and acceleration of the vehicle, and was accompanied by a video system to record license plates.

Measurements were conducted on December 31, 2002 and January 7, 8, and 31, 2003 in Denver. The measurement site was the interchange ramp from northbound I-25 to westbound 6th Avenue in central Denver. A database was compiled containing 21,321 records for which the State of Colorado provided make and model year information. These 21,321 records contained valid measurements for CO and CO₂. A total of 21,235 records contained valid measurements for CO, HC, and NO. The database, along with earlier databases and reports, can be found at www.feet.biochem.du.edu.

The mean CO, HC and NO emissions respectively for the fleet measured in this study were 0.35%, 88 ppm (offset adjusted – see below) and 456 ppm. These values are somewhat lower than the mean emissions for fleets measured by the University of Denver at the same site in the winters of 1996 and 1997, in separate studies, and in 1999, 2000 and 2001 as part of the current CRC study. The measured lower emissions can be attributed to the current fleet consisting of more modern vehicles with advanced emissions control systems.

As expected, the fleet emissions observed at the site in Denver exhibited a skewed distribution, with most of the total emissions contributed by a relatively small percentage of the measurements. For example, the cleanest 91% of the measurements are responsible for only 35% of CO emissions. This skewed distribution was also seen in previous studies at the site.

Using vehicle specific power, it was possible to adjust the emissions of the vehicle fleet measured in 2003 to match the vehicle driving patterns of the fleet measured in 1999, 2000, and 2001. After doing so, it was seen that the CO, HC, and NO emissions of the current year are lower than the previous years.

A model year adjustment was applied to a fleet of specific model year vehicles to track deterioration. The analysis indicated continued deterioration of model years measured in 1999. Tracking of model year fleets through five measurements in six years (including three years of this study) showed that the rate of emissions deterioration increases significantly after the vehicle has aged several years. An analysis of high emitting vehicles showed that there is considerable overlap of CO and HC high emitters, for instance 4.7% of the measurements contributed 40% of the total CO and 37% of the total HC. The noise in the CO and NO measurements was determined to be minimal, while noise in the HC channel was somewhat significant.

INTRODUCTION

Many cities in the United States are in violation of the air quality standards established by the Environmental Protection Agency (EPA). Carbon monoxide (CO) levels become elevated primarily due to direct emission of the gas, and ground-level ozone, a major component of urban smog, is produced by the photochemical reaction of nitrogen oxides (NO_x) and hydrocarbons (HC). As of 1998, on-road vehicles were estimated to be the single largest source for the major atmospheric pollutants, contributing 60% of the CO, 44% of the HC, and 31% of the NO_x to the national emission inventory.¹

According to Heywood,² carbon monoxide emissions from automobiles are at a maximum when the air/fuel ratio is rich of stoichiometric, and are caused solely by a lack of adequate air for complete combustion. Hydrocarbon emissions are also maximized with a rich air/fuel mixture, but are slightly more complex. When ignition occurs in the combustion chamber, the flame front cannot propagate within approximately one millimeter of the relatively cold cylinder wall. This results in a quench layer of unburned fuel mixture on the cylinder wall and in crevices, which is scraped off by the rising piston and sent out the exhaust manifold. With a rich air/fuel mixture, this quench layer simply becomes more concentrated in HC, and thus more HC is sent out the exhaust manifold by the rising piston. There is also the possibility of increased HC emissions with an extremely lean air/fuel mixture when a misfire occurs and an entire cylinder of unburned fuel mixture is emitted into the exhaust manifold. Nitric oxide (NO) emissions are maximized at high temperatures when the air/fuel mixture is slightly lean of stoichiometric, and are limited during rich combustion by a lack of excess oxygen and during extremely lean combustion by low flame temperatures. In most vehicles, practically all of the on-road NO_x is emitted in the form of NO.² Properly operating modern vehicles with three-way catalysts are capable of partially (or completely) converting engine-out CO, HC and NO emissions to CO₂, H₂O and N₂.²

Control measures to decrease mobile source emissions in non-attainment areas include inspection and maintenance (I/M) programs, oxygenated fuel mandates, and transportation control measures, but the effectiveness of these measures remains questionable. Many areas remain in non-attainment, and with the new 8-hour ozone standards introduced by the EPA in 1997, many locations still violating the standard may have great difficulty reaching attainment.³ In fact, Denver violated this standard on July 9, 2003 for the first time in many years.

The remote sensor used in this study was developed at the University of Denver for measuring the pollutants in motor vehicle exhaust, and has previously been described in the literature.^{4,5} The instrument consists of a non-dispersive infrared (IR) component for detecting carbon monoxide, carbon dioxide (CO₂) and hydrocarbons, and a dispersive ultraviolet (UV) spectrometer for measuring nitric oxide. The source and detector units are positioned on opposite sides of the road in a bi-static arrangement. Collinear beams of IR and UV light are passed across the roadway into the IR detection unit, and are then focused onto a dichroic beam splitter, which serves to separate the beams into their IR and UV components. The IR light is then passed onto a spinning polygon mirror that spreads the light across the four infrared detectors: CO, CO₂, HC and reference.

The UV light is reflected off the surface of the beam splitter and is focused into the end of a quartz fiber-optic cable, which transmits the light to an ultraviolet spectrometer. The UV unit is then capable of quantifying nitric oxide by measuring an absorbance band at 226.5 nm in the ultraviolet spectrum and comparing it to a calibration spectrum in the same region.

The exhaust plume path length and the density of the observed plume are highly variable from vehicle to vehicle, and are dependent upon, among other things, the height of the vehicle's exhaust pipe, wind, and turbulence behind the vehicle. For these reasons, the remote sensor can only directly measure ratios of CO, HC or NO to CO₂. The ratios of CO, HC, or NO to CO₂, termed Q, Q' and Q'' respectively, are constant for a given exhaust plume, and on their own are useful parameters for describing a hydrocarbon combustion system. The remote sensor used in this study reports the %CO, %HC and %NO in the exhaust gas, corrected for water and excess oxygen not used in combustion. The %HC measurement is a factor of two smaller than an equivalent measurement by an FID instrument.⁶ Thus, in order to calculate mass emissions the %HC values in the equations below would be RSD measured values multiplied by 2. These percent emissions can be directly converted into mass emissions per gallon by the equations shown below.

$$\begin{aligned} \text{gm CO/gallon} &= 5506 \times \% \text{CO} / (15 + 0.285 \times \% \text{CO} + 2.87 \times \% \text{HC}) \\ \text{gm HC/gallon} &= 8644 \times \% \text{HC} / (15 + 0.285 \times \% \text{CO} + 2.87 \times \% \text{HC}) \\ \text{gm NO/gallon} &= 5900 \times \% \text{NO} / (15 + 0.285 \times \% \text{CO} + 2.87 \times \% \text{HC}) \end{aligned}$$

These equations indicate that the relationship between concentrations of emissions to mass of emissions is almost linear, especially for CO and NO and at the typical low concentrations for HC. Thus, the percent difference in emissions calculated from the concentrations of pollutants reported here are equivalent to a difference calculated from the masses of the pollutants.

Another useful conversion is from percent emissions to g pollutant per kg of fuel. This conversion is achieved directly by first converting the pollutant ratio readings to the moles of pollutant per mole of carbon in the exhaust from the following equation:

$$\frac{\text{moles pollutant}}{\text{moles C}} = \frac{\text{pollutant}}{\text{CO} + \text{CO}_2 + 3\text{HC}} = \frac{(\text{pollutant}/\text{CO}_2)}{(\text{CO}/\text{CO}_2) + 1 + 6(\text{HC}/\text{CO}_2)} = \frac{(Q, 2Q', Q'')}{Q + 1 + 6Q'}$$

Next, moles of pollutant are converted to grams by multiplying by molecular weight (e.g., 44 g/mole for HC since propane is measured), and the moles of carbon in the exhaust are converted to kilograms by multiplying (the denominator) by 0.014 kg of fuel per mole of carbon in fuel, assuming gasoline is stoichiometrically CH₂. Again, the HC/CO₂ ratio must use two times the reported HC (as above) because the equation depends upon carbon mass balance and the NDIR HC reading is about half a total carbon FID reading.⁶

Quality assurance calibrations are performed as dictated in the field by atmospheric conditions and traffic volumes. A puff of gas containing certified amounts of CO, CO₂, propane and NO is released into the instrument's path, and the measured ratios from the

instrument are then compared to those certified by the cylinder manufacturer (Praxair). These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO₂ levels caused by atmospheric pressure and instrument path length. Since propane is used to calibrate the instrument, all hydrocarbon measurements reported by the remote sensor are given as propane equivalents.

Studies sponsored by the California Air Resources Board and General Motors Research Laboratories have shown that the remote sensor is capable of CO measurements that are correct to within $\pm 5\%$ for the values reported by an on-board gas analyzer, and within $\pm 15\%$ for HC.^{7,8} The NO channel used in this study has been extensively tested by the University of Denver, but we are still awaiting the opportunity to participate in an extensive blind study and instrument intercomparison to have it independently validated. Tests involving a late-model low-emitting vehicle indicate a detection limit ($\pm 3\sigma$) of 25 ppm for NO, with an error measurement of $\pm 5\%$ of the reading at higher concentrations. Appendix A gives a list of the criteria for valid/invalid data.

The remote sensor is accompanied by a video system to record a freeze-frame image of the license plate of each vehicle measured. The emissions information for the vehicle, as well as a time and date stamp, is also recorded on the video image. The images are stored on videotape, so that license plate information may be incorporated into the emissions database during post-processing. A device to measure the speed and acceleration of vehicles driving past the remote sensor was also used in this study. The system consists of a pair of infrared emitters and detectors (Banner Industries), which generate a pair of infrared beams passing across the road, 6 feet apart and approximately 2 feet above the surface. Vehicle speed is calculated from the time that passes between the front of the vehicle blocking the first and the second beam. To measure vehicle acceleration, a second speed is determined from the time that passes between the rear of the vehicle unblocking the first and the second beam. From these two speeds and the time difference between the two speed measurements, acceleration is calculated and reported in mph/s.

The purpose of this report is to describe the remote sensing measurements made in the Denver area, as part of CRC's E-23 program. Measurements were made on four days: December 31, 2002 and January 7, 8, and 31 of 2003. The measurement location used in this study was the interchange from northbound I-25 to westbound 6th Avenue in central Denver. A map of the measurement location is shown in Figure 1. This interchange ramp has an uphill grade of 8% (4.6°) at the measurement location. Measurements were generally made between the hours of 7:00 and 16:00. This was the fourth year of a multi-year study to characterize motor vehicle emissions and deterioration in the Denver area.

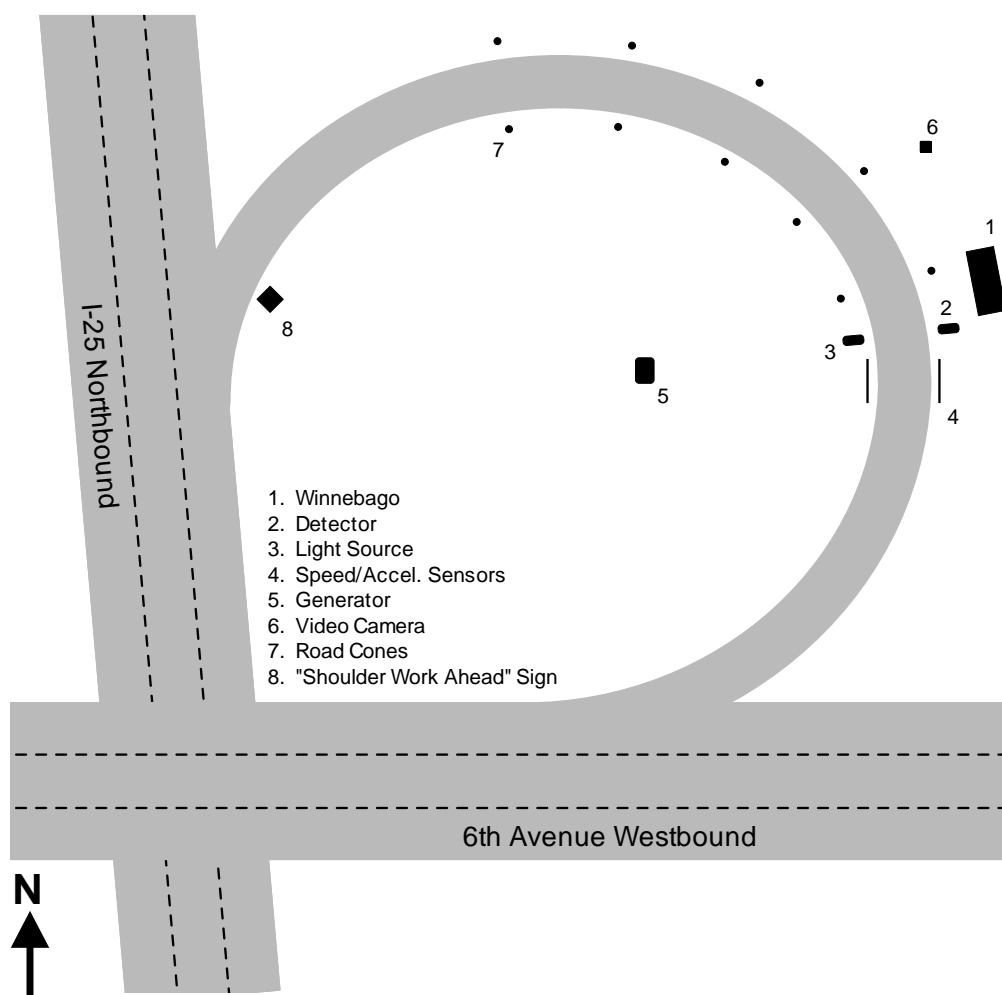


Figure 1. Area map of the interchange from I-25 northbound to 6th Avenue westbound in central Denver, showing remote sensor configuration and safety equipment.

RESULTS AND DISCUSSION

Following the four days of data collection in Denver, the videotapes were read for license plate identification. Plates that appeared to be in-state and readable were sent to the State of Colorado to be matched against registration records. The resulting database contained 21,321 records with registration information. Most of these records contain valid measurements for all gas species measured (see Table 1). The database can be found at www.feat.biochem.du.edu. The complete structure of the database and the definition of terms are included in Appendix C. The temperature and humidity record is included in Appendix A.

Table 1: Validity summary.

	CO	HC	NO
Attempted Measurements	28,172		
Valid Measurements	27,259	27,202	27,202
Percent of Attempts	96.8%	96.6%	96.6%
Submitted Plates	22,644	22,601	22,594
Percent of Attempts	80.4%	80.2%	80.2%
Percent of Valid Measurements	83.1%	83.1%	83.1%
Matched Plates	21,321	21,281	21,275
Percent of Attempts	75.7%	75.5%	75.5%
Percent of Valid Measurements	78.2%	78.2%	78.2%
Percent of Submitted Plates	94.2%	94.2%	94.2%

The validity of the attempted measurements is summarized in Table 1. The table describes the data reduction process beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration information. An attempted measurement is defined as a beam block followed by a half second of data collection. If the data collection period is interrupted by another beam block from a close following vehicle, the measurement attempt is aborted and an attempt is made at measuring the second vehicle. In this case, the beam block from the first vehicle is not recorded as an attempted measurement. Invalid measurement attempts arise when the vehicle plume is highly diluted, or the reported error in the ratio of the pollutant to CO₂ exceeds a preset limit. See Appendix A. The percent validity of the 2003 measurements is very similar to the validity seen in the previous years at this site, with approximately 75% of attempted measurements being valid and plate matched.

Table 2 is the data summary; included are summaries of previous remote sensing databases collected by the University of Denver at the I-25 and 6th Avenue site. The 1999, 2000, and 2001 measurements were conducted in December (of the previous year) and January (of that year) as parts of this multi-year CRC study. The measurements conducted in January of 1996 and 1997 were part of a separate study and are included here for comparison.

The average HC values here have been adjusted so as to remove an artificial offset in the measurements. This offset, restricted to the HC channel, has been reported in earlier CRC E-23-4 reports, but diagnosis has proved difficult. In the absence of a true diagnosis of the problem, we propose a remedy to remove the offset and obtain data which can be compared from the several years of study. This adjustment is to subtract a predetermined offset from the averaged data. The offset is determined as the mode (most frequent reading) of the emissions from the most recent model year. Since we assume these vehicles to emit next to nothing, such an approximation will only err slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year. However, this procedure will adjust the data so that measurements from different years can be compared.

The mode emissions for the three most recent model years 2001, 2002, and 2003 were all 20ppm. For the other Denver data sets, offsets were determined as the average emissions of the cleanest model year and make of vehicles from each data set. Offsets were determined to be 5, 60, and -50 for measurements conducted in 1999, 2000, and 2001, respectively. Offsets calculated for the two earlier reports are 70 and 100 ppm for 1996 and 1997. The offset subtraction has been performed here and later in the analysis where indicated.

Table 2. Data summary.

	2003	2001	2000	1999	1997	1996
Mean CO (%) (g/kg of fuel)	0.35 (44)	0.34 (43)	0.43 (54)	0.45 (56)	0.51	0.53
Median CO (%) (g/kg of fuel)	0.08 (11)	0.06 (8)	0.11 (15)	.09 (11.7)		
% of Total CO from Dirtiest 10% of Fleet	68.9	73.2	65.3	66.3	67.0	63.8
Mean HC (ppm) [†] (g/kg of fuel) [†]	88 (3.4)	112 (4.6)	115 (4.6)	125 (5.0)	160	180
Median HC (ppm) [†] (g/kg of fuel) [†]	40 (1.7)	80 (1.6)	50 (1.0)	75 (1.5)		
% of Total HC from Dirtiest 10% of Fleet [†]	74.8	77.2	77.6	66.0	72.5	77.5
Mean NO (ppm) (g/kg of fuel)	456 (6.5)	483 (6.8)	511 (7.2)	600 (8.4)	620*	860*
Median NO (ppm) (g/kg of fuel)	113 (1.6)	133 (1.9)	165 (2.3)	240 (3.4)		
% of Total NO from Dirtiest 10% of Fleet	53.5	51.7	48.4	44.6	43.6*	38.1*
Mean Model Year	1996.4	1994.6	1993.4	1992.4	1990.3	1989.2
Mean Speed (mph)	20.2	22.3	21.9	20.6	21.7	21.9
Mean Accel. (mph/s)	0.12	-0.77	0.08	0.21	0.11	-0.21
[†] These values have been HC offset adjusted as described in text.						
* Nitric oxide measurements until 1999 were made using a non-dispersive ultraviolet absorption NO channel. See Zhang <i>et al.</i> ⁹						

The table shows that fleet average emissions of each successive measurement is generally lower than the previous year. This trend is most likely due to a combination of technological advances in the emissions control systems of the modern fleet (and the removal of older technology vehicles from the fleet) and the fact that average age of the fleet has decreased during successive measurement campaigns with the exception of the most recent. As with other analyses in this report, however, such effects are suggested by

the data and can only be rigorously proved by further measurements. It should also be noted that the measurements conducted in 1996 and 1997 were made with a non-dispersive ultraviolet absorption nitric oxide channel, as described by Zhang *et al.*⁹ The instrument used in the current study, as in all studies conducted by the University of Denver under CRC's E-23 program, measures nitric oxide by dispersive ultraviolet absorption spectroscopy and is believed to offer a considerable improvement in measurement quality over the non-dispersive instrument.⁵

Table 3 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 21,042 records used in this fleet analysis, 16,491 (78%) were contributed by vehicles measured once, and the remaining 4551 (22%) records were from vehicles measured at least twice.

Table 3. Number of measurements on repeat vehicles.

Number of Times Measured	Number of Vehicles
1	14,513
2	1,471
3	339
4	52
4+	8
Total individual vehicles	16,383

Figure 2 shows the distribution of CO, HC and NO emissions by percent or ppm category from the data collected in this study. The solid bars show the percentage of the fleet in a given emissions category, and the gray bars show the percentage of the total emissions contributed by the given category. This figure illustrates the skewed nature of automobile emissions, showing that the lowest emission category is occupied by 75% of the fleet for NO and more than 91% of the fleet for CO. The fact that the cleanest 91% of the fleet is responsible for only 35% of the CO emissions further demonstrates how the emissions picture can be dominated by a small number of high-emitting readings and vehicles. The skewed distribution was also seen in the 1996, 1997, 1999, 2000, and 2001 data and is represented by the consistent high values of percent of total emissions from the dirtiest 10% of the measurements (See Table 2).

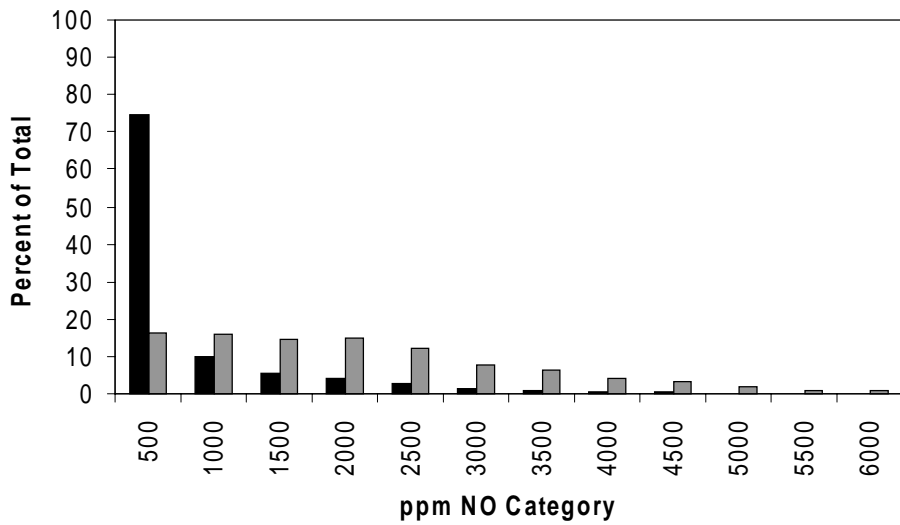
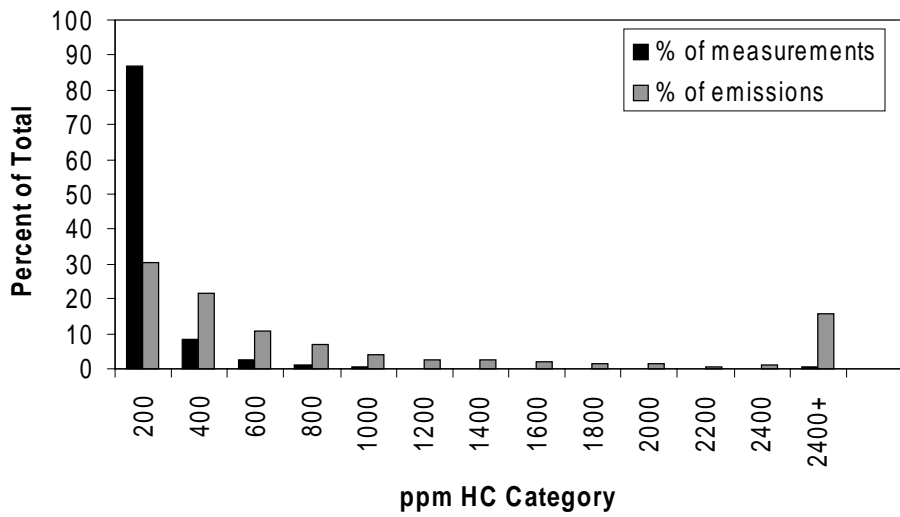
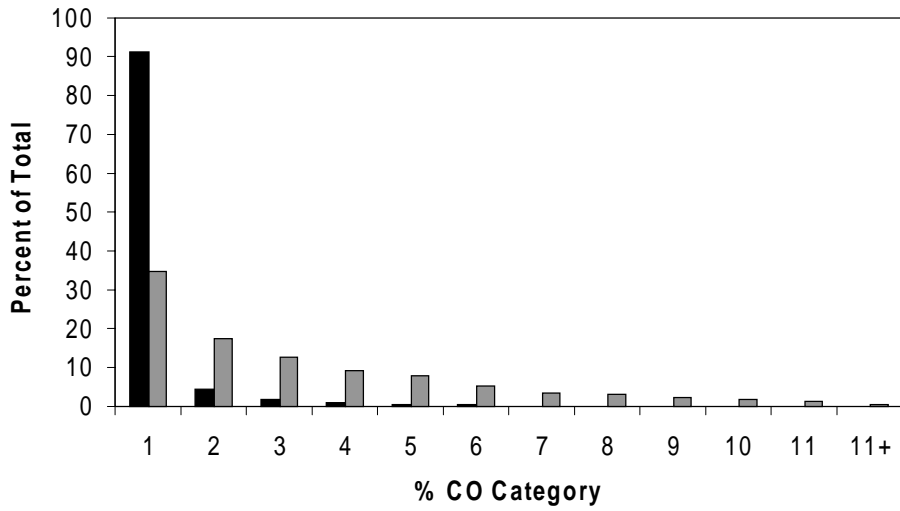


Figure 2. Emissions distribution showing the percentage of the measurements in a given emissions category (black bars) and the percentage of the total emissions contributed by the given category (gray bars).

The relationship between increasing vehicle emissions and older model years has been observed at a number of locations around the world, and Figure 3 shows that the fleet in the Denver area is not an exception.⁴ The plot of % NO vs. model year rises rather sharply, at least compared to the plots for CO and HC, and then appears to level out in model years prior to 1987. This has been observed previously,^{5,9} and is likely due to the tendency for older vehicles to lose compression and operate under fuel-rich conditions, both factors resulting in lower NO emissions. A further analysis of this phenomenon is added at the end of this report by normalizing to 1990 emissions levels.

As originally shown by Ashbaugh and Lawson,¹⁰ vehicle emissions by model year, with each model year divided into emission quintiles, were plotted for data collected in 2003. This resulted in the plots shown in Figure 4. The bars represent the mean emissions for each quintile, and do not account for the number of vehicles in each model year. This figure illustrates that the cleanest 40% of the vehicles, regardless of model year, make an essentially negligible contribution to the total fleet emissions. The large accumulations of negative emissions in the first two quintiles are the result of ever decreasing emission levels. Our instrument is designed such that when measuring a true zero emission plume, half of the readings will be negative and half will be positive. As the lowest emitting segments of the fleets continue to dive toward zero emissions, the negative emission readings will continue to grow toward half of the measurements. For HC the newest model years are nearly at that stage now.

An equation for determining the instantaneous power of an on-road vehicle has been proposed by Jimenez¹¹, which takes the form

$$VSP = 4.39 \cdot \sin(\text{slope}) \cdot v + 0.22 \cdot v \cdot a + 0.0954 \cdot v + 0.0000272 \cdot v^3$$

where VSP is the vehicle specific power in kW/metric tonne, *slope* is the slope of the roadway (in degrees), *v* is the vehicle speed in mph, and *a* is the vehicle acceleration in mph/s. Derived from dynamometer studies, and necessarily an approximation, the first term represents the work required to climb the gradient, the second term is the $f = ma$ work to accelerate the vehicle, the third is an estimated friction term, and the fourth term represents aerodynamic resistance. Using this equation, vehicle specific power was calculated for all measurements with valid speed and acceleration collected in the database. Figure 5 illustrates the emissions data when binned according to vehicle specific power with the upper limit of the bin equal to the label.

Here also, HC has been adjusted for the offset. The connected triangles in Figure 5 provide the number of measurements in each bin. Also shown in Figure 5 are vehicle emissions binned by specific power for remote sensing measurements collected in 1999, 2000, and 2001 at the same site. As expected, HC emissions show a negative dependence on vehicle specific power, while NO emissions show an overall positive dependence. An almost flat plot is seen from the CO emissions. The error bars included in the plot are standard errors of the mean. These uncertainties were generated for these γ -distributed data sets by applying the central limit theorem. Each day's average emission for a given VSP bin was assumed to be an independent measurement of the emissions at that VSP. Normal statistics were then applied to these daily averages. The increase of the CO and

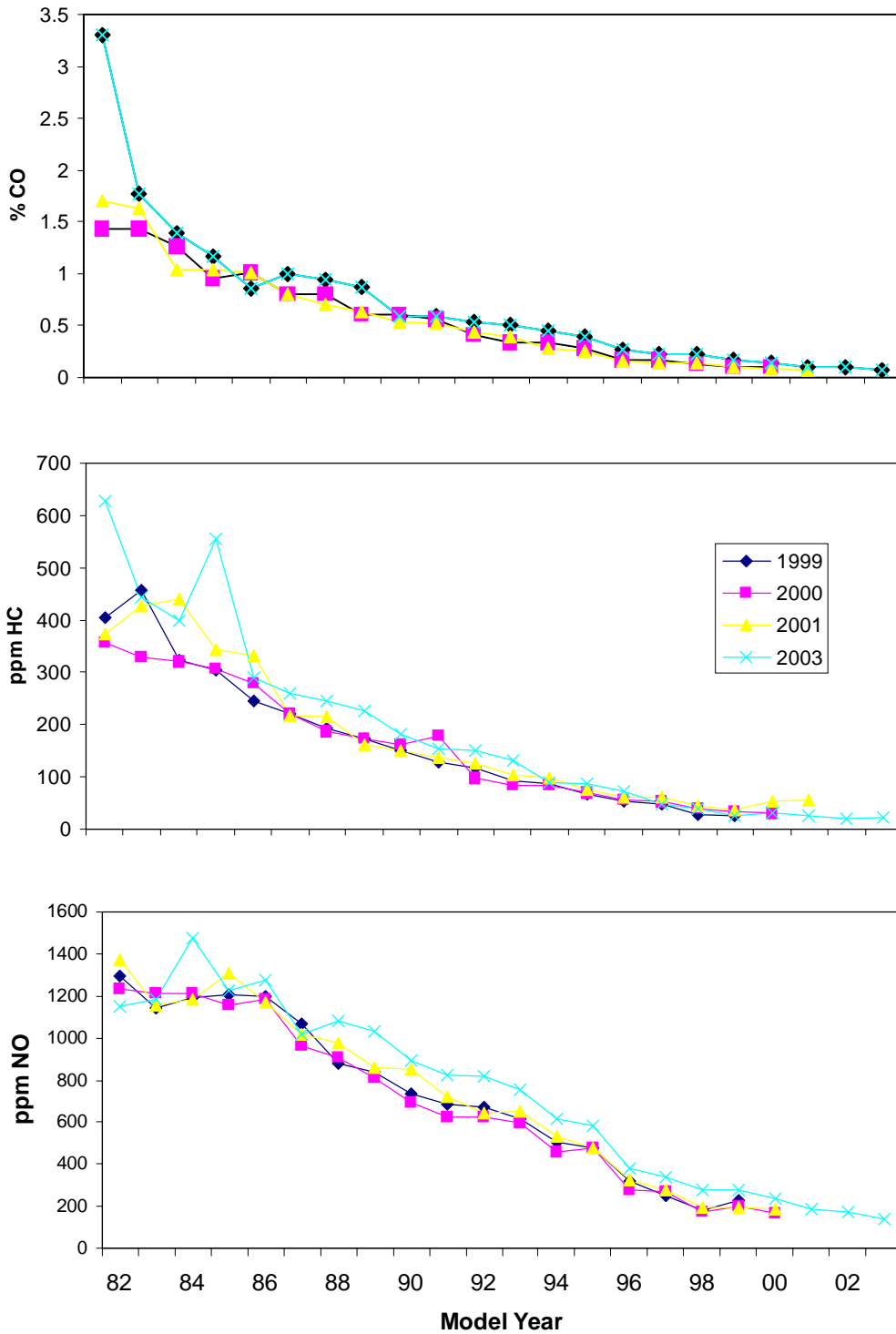


Figure 3. Mean vehicle emissions illustrated as a function of model year. Included are data from four years of measurement at this site.

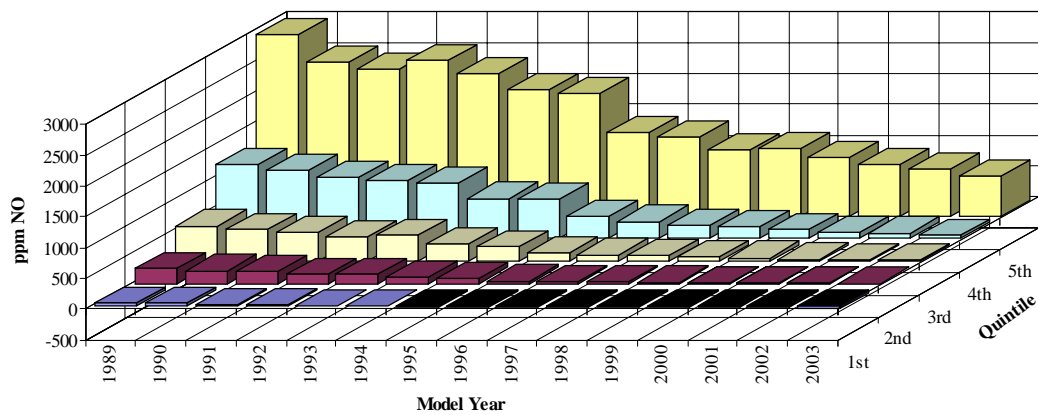
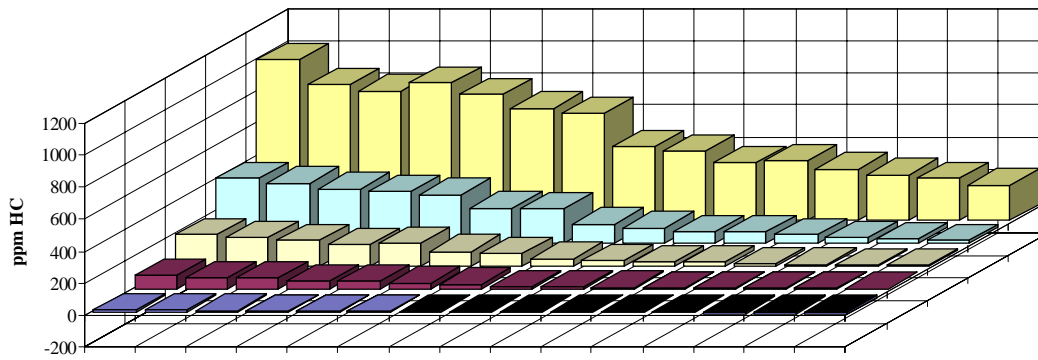
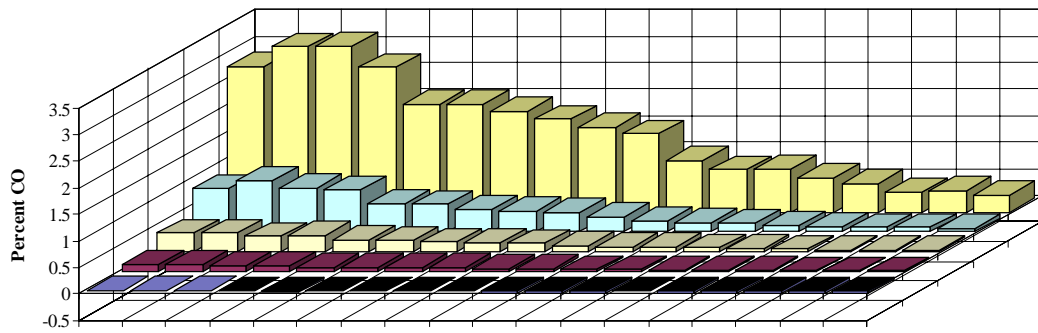


Figure 4. Vehicle emissions by model year, divided into quintiles.

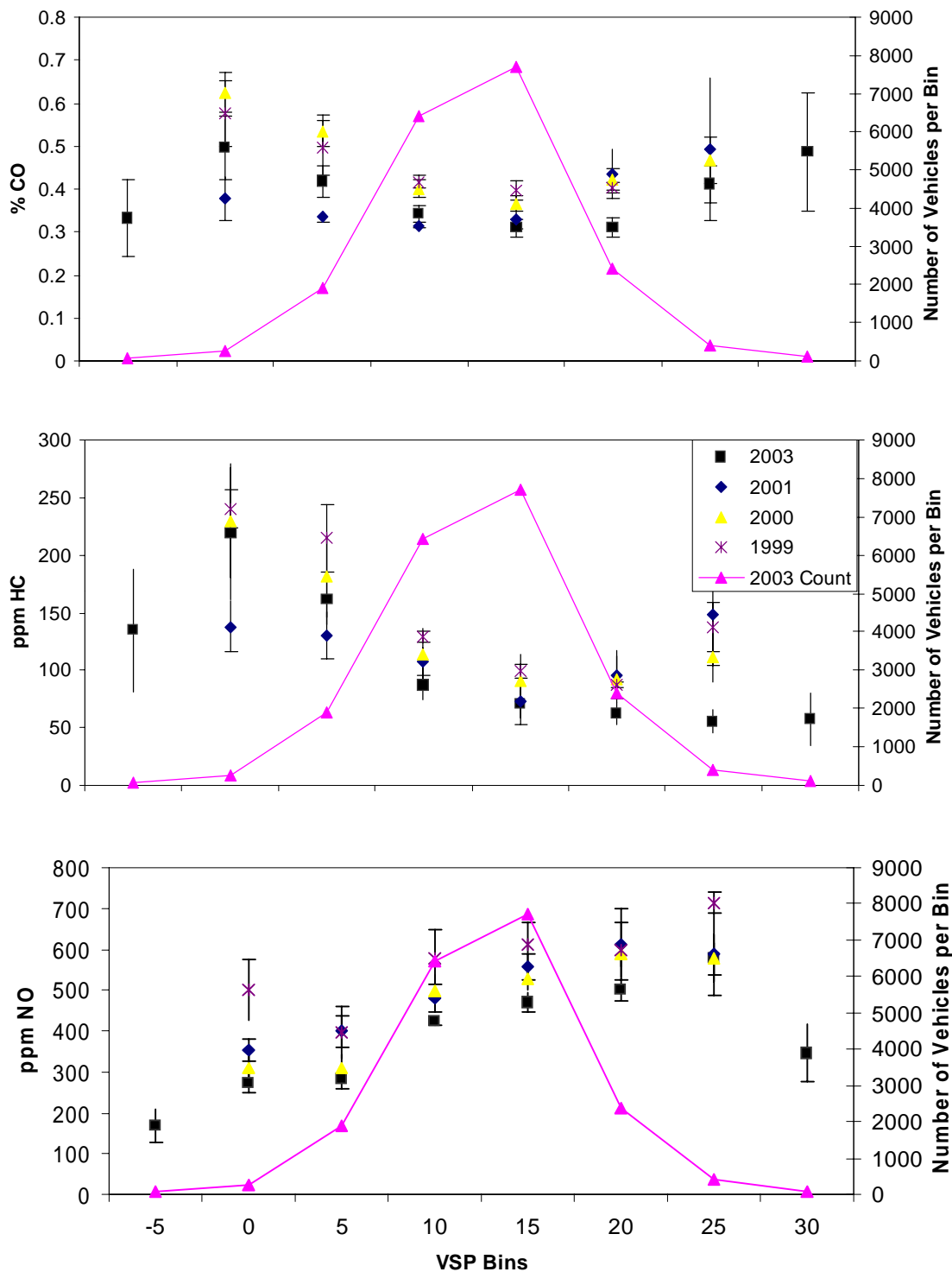


Figure 5. Vehicle emissions as a function of vehicle specific power. Data for the four years of study at this site are given, along with measurement counts for 2003 only. Error bars are 95% confidence intervals of the mean.

HC emissions measured in Denver at specific powers above 20 kW/tonne may be due to commanded power enrichment.

Using vehicle specific power, it is possible to reduce the influence of load and driving behavior from the mean vehicle emissions. Using only vehicles with all valid categories, Table 4 shows the mean emissions from vehicles in the 1999, 2000, 2001 and 2003 databases with specific powers between 0 and 25 kW/tonne. Note that these emissions do not vary considerably from the mean emissions for the entire databases, as shown in Table 2. Also shown in Table 4 are the mean emissions for the 2000, 2001, and 2003 measurements adjusted for specific power. This correction is accomplished by applying the mean vehicle emissions for each specific power bin in Figure 5 to the vehicle distribution, by specific power, for each bin from 1999. A sample calculation, for the specific power adjusted mean NO emissions in Chicago in 1998, is shown in Appendix D. Uncertainties are 95% confidence intervals of the mean of each individual day of measurement's average.

It can be seen from Table 4 that VSP adjustment does not eliminate the apparently low CO emissions in 2001. HC offset adjustment has been applied, and a small decreasing trend in the yearly adjusted averages is seen. These differences, however, are mostly within the observed uncertainties. In the case of NO, a trend is revealed as uncertainties mostly do not overlap. While working with the 2003 data, it was determined that earlier reports had not properly determined the standard errors of the mean. For this reason the values, especially the uncertainties, in Table 4 have been altered from the values reported in the previous years' reports.

Table 4. Specific power adjusted fleet emissions (0 to 25 kW/tonne only).

	1999	2000 (measured)	2000 (adjusted)	2001 (measured)	2001 (adjusted)	2003 (measured)	2003 (adjusted)
Mean CO (%)	0.42±.02	0.41±.02	0.41±.02	0.33±.01	0.34±.01	0.34±.02	0.34±.02
Mean HC (ppm)	124±6	112±22	111±22	109±13	96±11	86±11	92±12
Mean NO (ppm)	576±50	495±27	496±27	469±36	514±39	440±16	428±16

A correction similar to the VSP adjustment can be applied to a fleet of specific model year vehicles to look at deterioration of specific model year fleet averages, provided we use as a baseline only model years measured in the 1999 study. Table 5 shows the mean emissions for all vehicles from model year 1982 to 1999, as measured in 1999, 2000, 2001 and 2003. Applying the vehicle distribution by model year from 1999 to the mean emissions by model year from 2000, 2001, and 2003 yields the model year adjusted fleet emissions. HC offset correction has been applied. A sample calculation, for the model year adjusted mean NO emissions in Chicago in 1998, is shown in Appendix E. Uncertainties are again 95% confidence intervals calculated from daily averages. Though uncertainties overlap, the adjustments show that the decreases in total fleet average emissions of CO and HC seen during the current measurements are at least partially due to fleet turnover.

Table 5. Model year adjusted fleet emissions (MY 1982-1999 only).

	1999	2000 (measured)	2000 (adjusted)	2001 (measured)	2001 (adjusted)	2003 (measured)	2003 (adjusted)
Mean CO (%)	0.39±.0 2	0.38±.0 2	0.42±.0 2	0.34±.0 1	0.41±.0 2	0.43±.0 2	0.54±.0 3
Mean HC (ppm)	111±5	103±20	114±22	106±13	125±14	107±13	143±17
Mean NO (ppm)	568±49	500±27	544±30	514±39	589±45	573±23	681±27

Vehicle deterioration can also be illustrated by Figure 6, which shows the mean emissions of the 1982 to 2003 model year fleet as a function of vehicle age. Data from the 1996 and 1997 measurements are also included. The first point for each model year was measured in 1996, the second in 1997, the third in 1999, the fourth in 2000, the fifth in 2001 and the last point in 2003. Vehicle age was determined by the difference between the year of measurement and the vehicle model year. The most recent model years (up to 7 years old) show a small deterioration from one year to the next for all three pollutants. The deterioration rate seems to increase in the model years that are 8 years old and older (≤ 1991). This occurrence for HC and NO was also seen by McClintock in an analysis of IM240 I/M tailpipe test data.¹²

As expected, the CO and HC offset adjusted emissions show gradual increases for each model year as that year ages. The NO measurements also show a curious effect. The NO emissions of almost every model year measured in 1996 are significantly higher than in the other years of measurement. This is likely due to the fact that in 1996 and 1997 a non-dispersive method was used to measure NO. This instrument was less precise than the current instrument and most likely was measuring with an offset in 1996.⁵ Otherwise, NO emissions show a slow but steady deterioration with age, although the gap is evident between the 1996 model year and newer, and 1995 and older. This trend was also noticed in the CRC Chicago year 5 report.

Another use of the on-road remote sensing data is to predict the abundance of readings that are high emitting for more than one pollutant measured. One can look at the high CO emitters and calculate what percent of these are also high HC emitters, for example. This type of analysis would allow a calculation of maximum HC emission benefits resulting from fixing all high CO emitters. To this extent we have analyzed our data to determine what percent of the top decile of emitters of one pollutant are also in the top decile for another pollutant. These data are in Table 6; included in the analysis are only those vehicles that have valid readings for all three pollutants. The column heading is the pollutant whose top decile is being analyzed, and the values indicate what percentage of the fleet are high emitters only for the pollutants in the column and row headings. The values where the column and row headings are the same indicate the percentage that are high emitting in the one pollutant only. The "All" row gives the percentage of the fleet that is high emitting in all three pollutants.

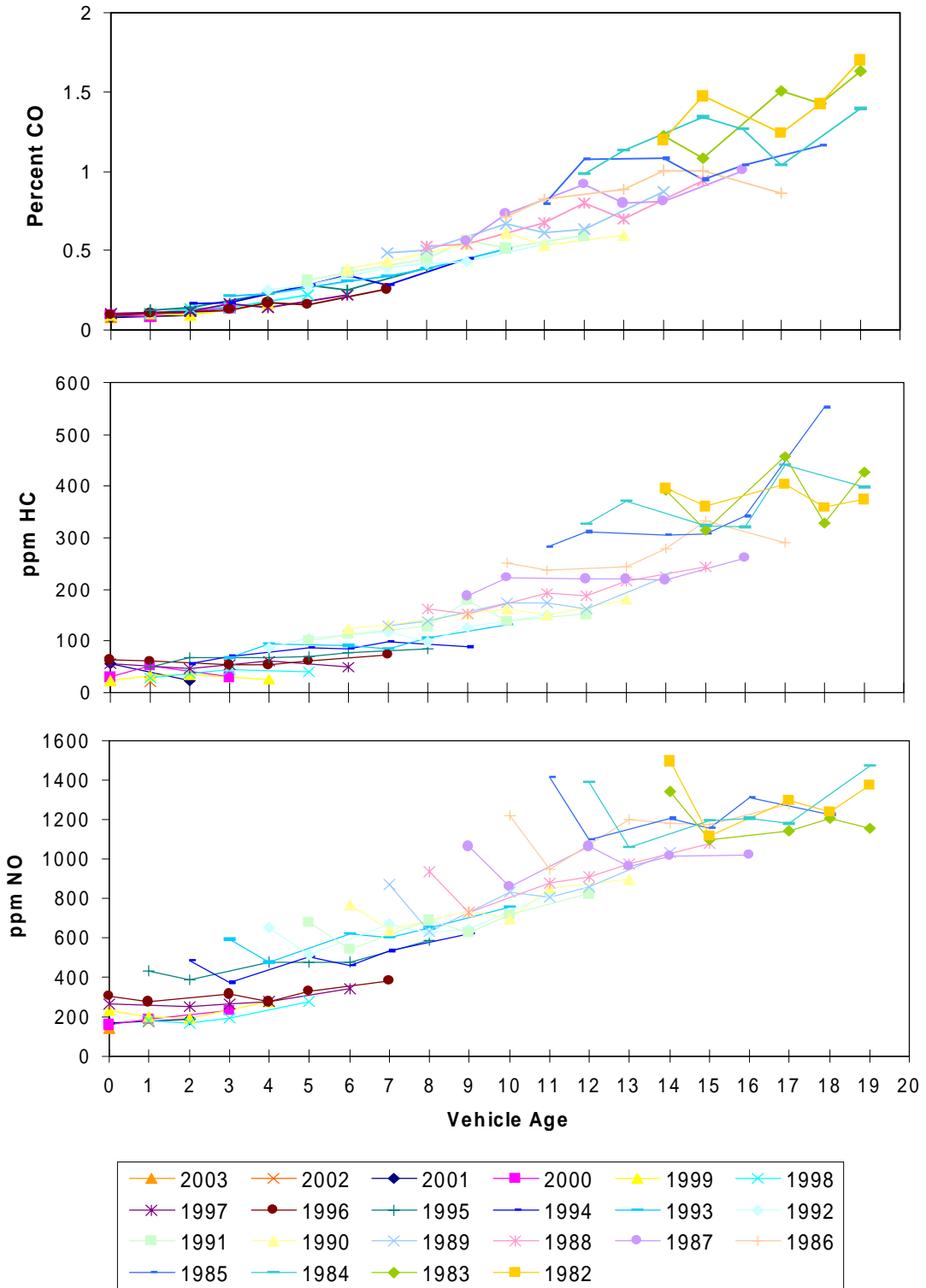


Figure 6. Mean vehicle emissions as a function of age, shown by model year.

Table 6: Percent of all vehicles that are high emitting.

Top 10% Decile	CO	HC	NO
CO	3.4%	4.7%	1.3%
HC	4.7%	2.3%	2.3%
NO	1.3%	2.3%	5.8%
All	0.7%	0.7%	0.7%

Thus, the table shows that 4.7% of the measurements are in the top decile for both HC and CO but not NO; 1.3% of the fleet is high emitting for CO and NO but not HC; 3.4% of the fleet are high CO emitters only.

The preceding analysis gives the percent of vehicle overlap but does not directly give emissions overlap. In order to assess the maximum emissions benefit of fixing all high emitting measurements of one or more pollutant, one must convert the Table 6 values to percent of emissions. Table 7 shows that identification of all vehicles that are high emitting for CO would identify an overall 39.4% of HC and 6.6% of NO reduction. More efficiently, identification of the 4.7% high CO and HC measurements accounts for 42% of the total CO and 39% of the total on-road HC. HC offset correction has been applied.

Table 7: Percent of total emissions from high emitting vehicles.

Top 10% Decile	CO	HC	NO
CO	17.2%	39.4%	6.6%
HC	41.7%	12.7%	13.3%
NO	5.9%	15.6%	28.9%
All	4.1%	7.1%	4.7%

In the manner described in the Phoenix, Year 2 report¹³, instrument noise was measured by looking at the logarithmic slope of the negative portion of the emissions distribution functions. Such plots were constructed for the three pollutants. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor. The Laplace factor describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors were found to be 0.05, 0.008 and 0.007 for CO, HC and NO, respectively. These values indicate standard deviations of 0.07%, 108 ppm and 92 ppm for individual measurements of CO, HC and NO, respectively. In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per bin, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages reduce to 0.007%, 11 ppm and 9 ppm, respectively.

A new way to look at emissions versus model year was attempted with this data set. The 2003 emissions by model year shown in Figure 4 were normalized to 1990 = 1 (arbitrary unit). Figure 7 shows the resulting plot for all three pollutants. CO and HC increase sharply while NO levels out as vehicles of model years older than 1989 are observed. We believe that this is expected behavior and is caused by an increasing fraction of the older model year operating on the rich side of stoichiometry, a phenomenon expected to raise CO and HC, while lowering NO.² Lower NO is a result of lower combustion temperature and, most importantly, lack of oxygen to react with N₂. Figure 8 shows on an expanded scale, only the normalized data from the 1990 model year forwards. In this graph it is apparent that NO and CO track closely with model year and HC is similar except for an apparent “flat” spot for the newest model years. This view leads us to believe that our previous contention that NO tended to jump ahead of CO and HC amongst newer model year, then level off was false. The impression was caused by the auto scaling from the high tail of HC and CO and not NO. In this view, NO, HC, and CO emissions versus model year are seen to closely correlate (not anticorrelate as in the oldest model year). We believe that this indicates progressively poorer emission control, however, in a fleet of vehicles fundamentally operating close to stoichiometry. One is tempted to ascribe this observation to catalyst “deterioration”, but with a single time slice, this contention cannot be unequivocally supported. We anticipate further analysis in this “new” look.

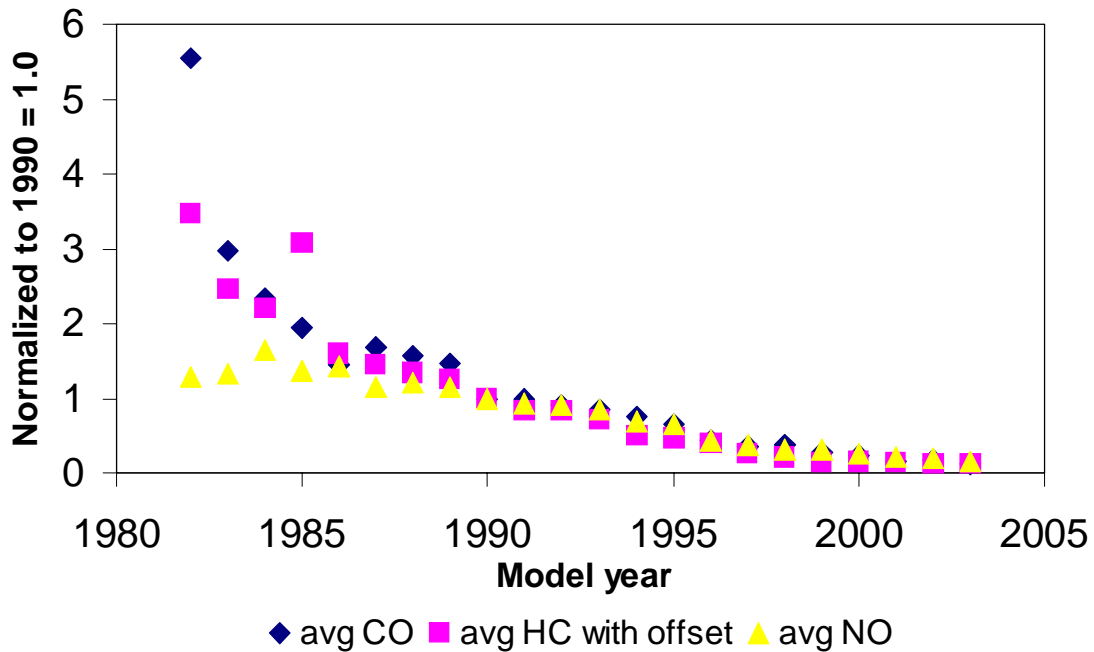


Figure 7. Average emission data by model year, normalized to 1990 emissions.

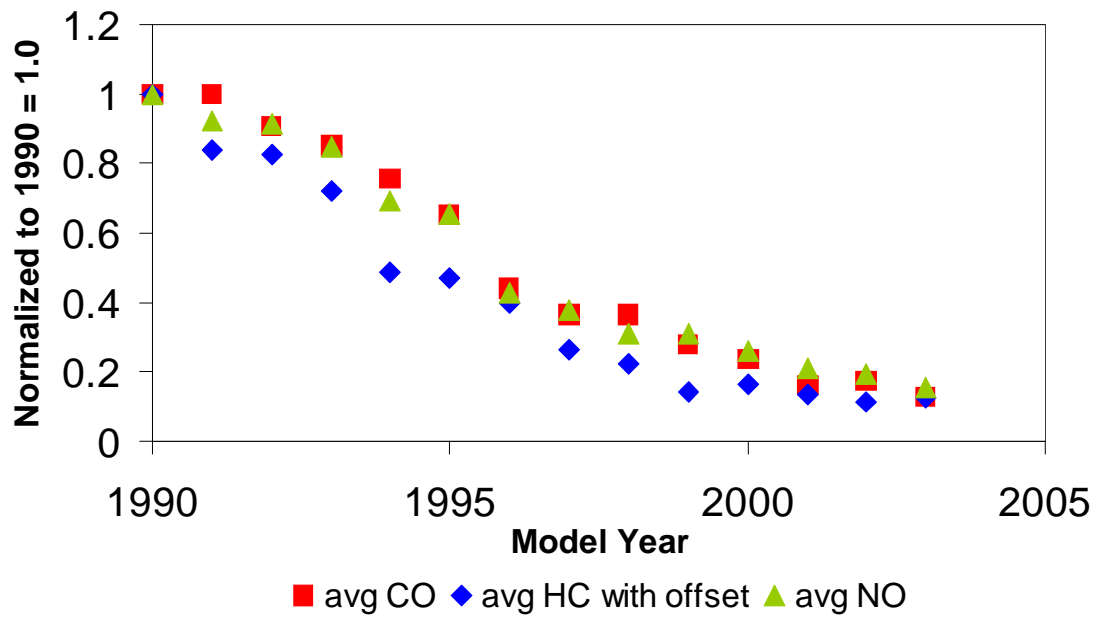


Figure 8. Average emission data by model year since 1990, normalized to 1990 emissions = 1.0.

CONCLUSIONS

The University of Denver has completed the fourth year of a multi-year remote sensing study of motor vehicle emissions and deterioration in the Denver area. Four days of fieldwork in late December 2002 and January 2003 were conducted on an uphill interchange ramp from northbound I-25 to westbound 6th Avenue in central Denver. A database was compiled containing 21,321 records for which the State of Colorado provided make, model year and I/M status information. Of these records 21,235 contained valid measurements for all gases measured.

The mean CO, HC and NO emissions for the fleet measured in this study were 0.35%, 88 ppm (offset adjusted) and 456 ppm, respectively with an average model year of 1994.6. The fleet emissions observed at the site in Denver exhibited a skewed distribution, with the dirtiest 10 % of the fleet contributing 69%, 75% and 54% of the CO, HC and NO emissions, respectively. An analysis of the emissions as a function of model year showed a typical inverse relationship. Measured emissions as a function of vehicle specific power supported the finding that HC and CO show a negative correlation while NO shows a positive one.

Having collected data for four out of five years at the same time and location, it was possible to show the deterioration of a specific model year fleet from one year to the next. It was seen that more recent model year vehicles have lower CO and HC emissions almost independent of age. An analysis of high emitting measurements showed that there is considerable CO and HC overlap. Continuing studies at the same site should allow further insight to be gained as to the effects of deterioration on motor vehicle emissions from one year to the next. Data are available on the web at www.feat.biochem.du.edu for the 2003 and previous studies. Appendix C defines the database format.

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APPENDIX A: FEAT criteria to render a reading not measured or “invalid”.

Not measured:

- 1) “Vehicle” with less than 0.5 seconds clear to the rear. Often caused by elevated pickups and trailers causing a “restart” and renewed attempt to measure exhaust. The restart number appears in the data base.
- 2) Vehicle which drives completely through during the 0.4 seconds “thinking” time (relatively rare).

Invalid :

- 1) Insufficient plume to rear of vehicle relative to cleanest air observed in front or in the rear; at least five, 10ms averages $>200\text{ppm.m CO}_2$ or $>400\text{ppm.m CO}$. (0.25 % CO_2 or 0.5% CO in an 8 cm cell. This is equivalent to the units used for CO_2 max.) Often HD diesel trucks, bicycles.
- 2) Too high error on CO/CO_2 slope, equivalent to $\pm 20\%$ for %CO. >1.0 , 0.2%CO for %CO <1.0 .
- 3) Reported %CO , $<-1\%$ or $>21\%$. All gases invalid in these cases.
- 4) Too high error on HC/CO_2 slope, equivalent to $\pm 20\%$ for HC $>2500\text{ppm}$ propane, 500ppm propane for HC $<2500\text{ppm}$.
- 5) Reported HC $<-1000\text{ppm}$ propane or $>40,000\text{ppm}$. HC “invalid”.
- 6) Too high error on NO/CO_2 slope, equivalent to $\pm 20\%$ for NO $>1500\text{ppm}$, 300ppm for NO $<1500\text{ppm}$.
- 7) Reported NO $<-700\text{ppm}$ or $>7000\text{ppm}$. NO “invalid”.

Speed/Acceleration valid only if at least two blocks and two unblocks in the time buffer and all blocks occur before all unblocks on each sensor and the number of blocks and unblocks is equal on each sensor and $100\text{mph}>\text{speed}>5\text{mph}$ and $14\text{mph/s}>\text{accel}>-13\text{mph/s}$ and there are no restarts, or there is one restart and exactly two blocks and unblocks in the time buffer.

APPENDIX B: Temperature data.

1999		
Date	Time	Temp. (°F)
01/14	1416	57
	1550	56
01/15	0925	47
	0945	48
	1024	58
	1108	58
	1125	58
01/18	0830	40
	0930	45
	1020	50
	1050	55
	1130	50
	1200	46
02/01	0800	26
	0833	30
	0911	33
	0929	33
	1000	40
	1025	46
	1107	54
	1156	55

2000			
Date	Time	Temp. (°F)	Humid. (%RH)
12/30	1123	48	38
	1203	51	32
	1306	54	29
	1402	55	28
	1514	64	26
	1600	57	26
	1654	52	27
01/11	0933	54	38
	1033	54	32
	1150	55	28
	1233	52	30
	1337	49	37
	1437	50	39
	1551	49	41
	1607	48	41
01/13	0843	35	61
	0943	35	61
	1042	35	62
	1102	36	61
	1201	39	59
	1309	41	56
	1411	42	52
	1509	45	48
01/14	0753	32	69
	0842	35	65
	0953	43	50
	1115	51	36

2001			
Date	Time	Temp. (°F)	Humid. (%RH)
1/5	7:42	32.5	60
	8:57	73.2	59
	9:45	42.5	51
	11:49	59.1	28
	13:05	64	24
	14:10	66.3	20
1/6	7:12	41.3	44
	8:13	42.2	46
	10:12	49.8	38
	11:30	50.6	38
	12:30	52.4	37
	13:33	61	21
	14:43	61	<20
	15:47	61	25
1/8	7:50	26.8	38
	8:57	53.4*	24*
	10:18	43	28
	11:19	46.4	24
	12:27	50.9	21
	13:27	53.1	<20
	14:27	53.8	<20
	15:27	53.3	<20

*Inaccurate measurements due to direct sunlight

2002/2003			
Date	Time	Temp. (°F)	Humid (%RH)
12/31/02	0945	34	31
	1045	39	30
	1119	43	29
	1138	41	29
	1238	50	26
	1316	50	26
	1416	52	26
	1516	52	26
	1600	48	27
1/7/03	0905	43	38
	1009	48	36
	1109	54	30
	1212	59	25
	1239	61	21
	1309	64	18
	1409	66	15
	1509	68	15
	1602	66	15
1/8/03	0927	48	32
	1040	57	26
	1116	61	25
	1216	68	17
	1317	70	14
	1419	73	11
	1525	68	15
	1550	66	15
1/31/03	1015	55	37
	1115	64	31
	1203	63	26
	1215	64	24
	1315	64	24

Appendix C: Explanation of the den_2003.dbf database.

The den_2003.dbf is a Microsoft Foxpro database file, and can be opened by any version of MS Foxpro, regardless of platform. The following is an explanation of the data fields found in this database:

License	Colorado license plate
Date	Date of measurement, in standard format.
Time	Time of measurement, in standard format.
Percent_co	Carbon monoxide concentration, in percent.
Co_err	Standard error of the carbon monoxide measurement.
Percent_hc	Hydrocarbon concentration (propane equivalents), in percent.
Hc_err	Standard error of the hydrocarbon measurement.
Percent_no	Nitric oxide concentration, in percent.
No_err	Standard error of the nitric oxide measurement.
Percent_co2	Carbon dioxide concentration, in percent.
Co2_err	Standard error of the carbon dioxide measurement.
Opacity	Opacity measurement, in percent.
Opac_err	Standard error of the opacity measurement.
Restart	Number of times data collection is interrupted and restarted by a close-following vehicle, or the rear wheels of tractor trailer.
CO2_flag	Indicates a valid carbon dioxide measurement by a “V”, invalid by an “X”.
CO_flag	Indicates a valid carbon monoxide measurement by a “V”, invalid by an “X”.
Hc_flag	Indicates a valid hydrocarbon measurement by a “V”, invalid by an “X”.
No_flag	Indicates a valid nitric oxide measurement by a “V”, invalid by an “X”.
Opac_flag	Indicates a valid opacity measurement by a “V”, invalid by an “X”.
Max_co2	Reports the highest absolute concentration of carbon dioxide measured by the remote sensor; indicates the strength of the observed plume. Units are %CO ₂ as measured in an 8 cm cell.
Speed_flag	Indicates a valid speed measurement by a “V”, an invalid by an “X”.
Speed	Measured speed of the vehicle, in mph.
Accel	Measured acceleration of the vehicle, in mph/s.
Ref_factor	Reference detector voltage. Used along with “CO2_factor” to observe calibration shifts.
CO2_factor	CO ₂ detector voltage. Used along with “Ref_factor” to observe calibration

	shifts.
Veh_type	Type of vehicle.
Vin	Vehicle identification number.
Year	Model year of the vehicle.
Make	Manufacturer of the vehicle.
Model	Model name of the vehicle.
Body	Body style of the vehicle.
Series	Series code of vehicle.
Fuel	Fuel type: 'G' indicates gasoline, 'D' indicates diesel.
Gvw	Gross vehicle weight?
Legl_city	City the vehicle resides in.
Legal_St	State the vehicle resides in.
Legl_zip5	Zip code the vehicle resides in.
Mail_City	City of owner mailing address.
Mail_St	State of owner mailing address.
Mail_zip5	Zip code of owner mailing address.
County	County code where vehicle resides.
Urbn_rl_cd	Urban or rural designation where vehicle resides. 'R' is rural and 'U' is urban.
Bus_Date	Unknown.
Expire_Date	Date that current vehicle registration expires.
Purch_Date	Date vehicle was purchased.
Msrp	Manufacturer suggested retail price in US\$.
Odometer	Odometer reading during I/M inspection.
Emiss_flag	I/M flag: 'Y', 'N', 'X'.
E_Status	I/M status: 'P' is pass and 'E' is exempt.
Prog_Type	I/M type: 'E' is enhanced and 'B' is basic.
Test_date	I/M test date.
Next_insp	Due date for next inspection.

**APPENDIX D: Calculation of Vehicle Specific Power Adjusted
Vehicle Emissions (Chicago 1997-8 data)**

1997 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	247	228	56316
	-2.5	235	612	143820
	0	235	1506	353910
	2.5	285	2369	675165
	5	352	2972	1046144
	7.5	426	3285	1399410
	10	481	2546	1224626
	12.5	548	1486	814328
	15	598	624	373152
	17.5	572	241	137852
	20	618	92	56856
			15961	6281579
		Mean NO (ppm)	394	
1998 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	171	126	21546
	-2.5	231	259	59829
	0	252	753	189756
	2.5	246	1708	420168
	5	316	2369	748604
	7.5	374	3378	1263372
	10	418	3628	1516504
	12.5	470	3277	1540190
	15	487	2260	1100620
	17.5	481	1303	626743
	20	526	683	359258
			19744	7846590
		Mean NO (ppm)	397	
1998 (Adjusted)	VSP Bin	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	-5	171	228	38988
	-2.5	231	612	141372
	0	252	1506	379512
	2.5	246	2369	582774
	5	316	2972	939152
	7.5	374	3285	1228590
	10	418	2546	1064228
	12.5	470	1486	698420
	15	487	624	303888
	17.5	481	241	115921
	20	526	92	48392
			15961	5541237
		Mean NO (ppm)	347	

APPENDIX E: Calculation of Model Year Adjusted Fleet Emissions (Chicago 1997-8 data)

1997 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	690	398	274620
	84	720	223	160560
	85	680	340	231200
	86	670	513	343710
	87	690	588	405720
	88	650	734	477100
	89	610	963	587430
	90	540	962	519480
	91	500	1133	566500
	92	450	1294	582300
	93	460	1533	705180
	94	370	1883	696710
	95	340	2400	816000
	96	230	2275	523250
97	150	2509	376350	
			17748	7266110
		Mean NO (ppm)		409
1998 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	740	371	274540
	84	741	191	141531
	85	746	331	246926
	86	724	472	341728
	87	775	557	431675
	88	754	835	629590
	89	687	1036	711732
	90	687	1136	780432
	91	611	1266	773526
	92	538	1541	829058
	93	543	1816	986088
	94	418	2154	900372
	95	343	2679	918897
	96	220	2620	576400
97	177	3166	560382	
			20171	9102877
		Mean NO (ppm)		451
1998 (Adjusted)	Model Year	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	83	740	398	294520
	84	741	223	165243
	85	746	340	253640
	86	724	513	371412
	87	775	588	455700
	88	754	734	553436
	89	687	963	661581
	90	687	962	660894
	91	611	1133	692263
	92	538	1294	696172
	93	543	1533	832419
	94	418	1883	787094
	95	343	2400	823200
	96	220	2275	500500
97	177	2509	444093	
			17748	8192167
		Mean NO (ppm)		462

APPENDIX F: Field Calibration Record.

Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
12/31	11:14	1.33	1.44	2.22
12/31	13:09	1.258	1.204	1.733
1/7	10:00	1.342	1.204	1.443
1/7	12:35	0.974	0.939	1.084
1/7	15:12	1.157	1.158	1.277
1/8	9:15	1.237	1.191	1.834
1/8	11:10	0.97	1.096	1.493
1/31	10:00	1.124	1.084	1.567
1/31	12:00	0.912	0.932	1.257